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Prevalence of pesticides in postconsumer agrochemical polymeric packaging

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Abstract

Pesticide remains contained in agrochemical packaging waste are a source of uncontrolled risk for human health; they are also a quality feedstock for the plastic recycling industry. Many governments have recently started to establish laws and regulations to develop systems for recovering and recycling the polymeric packages used for pesticides. There is also a demand in having a procedure to control the suitability of the pesticide packages to be reused. We have developed a two-step operation process to assess the pesticide residues in agricultural containers made of a variety of polymeric matrices. The procedure is based on an extraction with a solvent mixture followed by UPLC-MS/MS determination. Solvents for neutral pesticides were selected considering the Hildebrand solubility (δ) of solvents and polymers together with those estimated for the pesticides. The proposed technique is effective in recovering imbibed pesticides in polymeric matrices. Also, a simplified extraction procedure has been tested to become a routine method for these wastes. We have found that in many cases a significant amount of pesticides remain into the polymeric matrix, even after a standardized cleaning; the impact of releasing these hazardous compounds into the environment is to be of further consideration.

Keywords

Circular economy; environmental contamination; recycling.

1. **Introduction**

Recycling, both in developed and developing countries, is currently essential without debate. Strong economic and environmental factors have prompted governments, enterprises, and individuals to embrace practices that favour the reuse of materials, recognized to be a pillar for circular economy.

Polymeric materials, because of their origin—mainly oil—and their persistence in the environment, are, together with glass, paper and metal, amongst the materials most widely recycled. The pre-separation of polymeric material on the basis of its composition, followed by cleaning and conditioning, enables a large amount of these materials—6.63 Mt in Europe alone—to be returned to the production system (Leslie et al., 2016 and Plastics Europe, 2015).

However, while some residues are more suitable for energy recovery, others pose specific difficulties with respect to recycling. Polymeric waste products in direct contact with hazardous substances (e.g., medical plastic waste) cannot be recycled and are incinerated (Zhao et al., 2009). Similar difficulties are encountered with the residual containers of pesticides. Pesticides are commercially distributed to consumers in many types of containers, the most widely used of which are composed by a polymer or copolymer or coated polymer. Traditionally, consumers have recklessly dumped these containers into the environment, burned them, or buried them. Such practices directly contribute to environmental contamination and pose a public health risk. Overall, pesticides have been recently recognized as one of the six world's worst pollution problems affecting human health (Pure Earth, 2015).

In recent years, following the principles of circular economy, many governments and public institutions have started to pass laws and establish regulations to develop systems for recovering and recycling the polymeric containers used for pesticides. The EU has established criteria that render a waste hazardous and delineate the limits of the concentration of hazardous substances in this waste for it to be acceptable for recycling (EC, CD 2001/118/EC, 2001). Moreover, it has deployed regulations (EC, CD 2009/128/EC, 2009) on which many countries base their national legislation (CropLife International aisbl, 2015 and Spanish RD 1311/2012, 2012) regarding the methods applied to recover hazardous waste containers. Accordingly, a European Project, AgroChePack, 2013 and Briassoulis et al., 2014, has recently developed an optimized agrochemical plastic packaging waste (APPW) management scheme. It highlights the role of the farmer in decontaminating the container after use as one of the most critical issues of the existing schemes. Briefly, the farmer has to manually triple rinse or

pressure rinse the empty container with water, ensuring that the rinsate runs into the tank and that the container is stored in large bags, referred as “big bags”. It is assumed that after this treatment the container is no longer hazardous and thus it is suitable for recycling because the pesticide levels are expected to be below the thresholds established by regulations (ECPA, 2015). Once the container reaches the APPW management system, the non-dangerous nature of the final residue needs to be ensured before it is allowed back into the market. Some aspects are to be considered, firstly the precise levels of pesticide in the container after the correct application of triple rinse. Secondly, the convenience of the residue limits established depending on the future use of the recycled material. Thirdly, connected with the second aspect, the traceability in the use of recycled materials made from containers of pesticides.

This situation is not by any means a trivial problem. Some countries use this material in a closed cycle for applications that are not in direct contact with humans or animals (e.g., drains and building material). However, in many countries where national pesticide container management schemes are absent, appropriate use of the recycled material is not guaranteed, and the possibility of finding a significant concentration of pesticides in polymeric-made objects for personal use must be considered (Leslie et al., 2016).

Under these premises, it is pertinent to establish a control system over the mentioned materials, especially when they could be incorporated into products for general use. Although methods for determining the additives in polymers have been developed (Bart, 2005 and Bolgar, 2015), we have no knowledge of the availability of public methods to analyse the pesticide contents in plastic container residues. Previous studies have focused only on determining pesticides in the aqueous rinsate from plastic containers (EPA, 1992 and EPA, 2008). However, the amount of pesticide that remains adsorbed and absorbed onto the walls of these receptacles is still a major issue. In the case of residual agricultural films (Nerín et al., 1997), pesticides remain in the material matrix. The need for approaches to address this concern was identified some years ago (EPA, 1992) and still remains the focus of debate (Briassoulis et al., 2014). In this regard, only a few private companies have developed techniques to address pesticide packaging security; however, these are for internal use, and they are focused mainly on their own products (ECPA, 2015 and EPA, 1992).

The aim of the present work is to develop a procedure to asses for the pesticide residues in a variety of polymeric matrices used for pesticide containers. In addition, the technique is applied to quantify the pesticide residues remaining in empty triple-

rinsed containers; which even in the case they were under the threshold legal levels of hazardousness, are not to be neglected for the traceability of the recycling from these containers. The proposed technique is intended to be easily implemented using materials and solvents common in an environmental laboratory as a routine method for these samples.

2. Material and Methods

2.1 Reagents and solvents

The following 18 pesticide standards were used: Acetochlor, carfentrazone-ethyl, cypermethrin, desmedipham, dimethoate, ethofumesate, fluometuron, glyphosate trimesium, lufenuron, nicosulfuron, pendimethalin, phenmedipham, propargite, pyraflufen-ethyl, quizalofop-P-ethyl, quizalofop-P-tefuryl, sulcotrione and terbuthylazine. All standards were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany), and they had a purity 95% or greater (typically >99%). The methanol >99.8%, acetone >99.5% and dichloromethane >99.9% were sourced from Sigma-Aldrich (Sigma-Aldrich, Madrid, Spain). The water was Milli-Q quality (Millipore, Madrid, Spain). Acetonitrile was purchased from J.T. Baker (Quimega, Lleida, Spain).

2.2 Sample preparation and extraction of pesticides

Six pesticides, cypermethrin, dimethoate, glyphosate isopropylamine (referred hereon as glyphosate), imazamox ammonium salt (referred hereon as imazamox), nicosulfuron and pendimethalin (Table 1), were selected to optimize the extraction step. Three identical, commercially available bottles of the same batch of each pesticide were acquired from an agronomical cooperative in Lleida, Spain. The bottles were composed by polymeric material and contained 1000 mL of pesticide. These pesticides were chosen because of their wide use in crop production, their very different polarities, their presence in various types of polymeric packaging and their commercial availability. Each bottle was emptied and subjected to a consecutive triple rinse with 250 mL of fresh distilled water per rinse. Next, the caps were discarded, and the bottles were left upside down on a metal grid to drain and dry uniformly at room temperature. Each bottle was then cut longitudinally into two equal halves: A and B. For each half, a 1-cm wide strip was set apart, A' and B' (Figure 1); the A' strips were reserved to be dissolved by an alternative extraction procedure, whereas the B' strips were for the counter-analysis. All strips were weighed separately.

Except for the two strips, the A and B halves were cut into small pieces of approximately 1 x 1 cm with scissors, and the pieces were stored in glass beakers. The pieces corresponding to half B were reserved for performing a simplified extraction as detailed in Results and Discussion section. The pieces of half A were transferred to 500-mL borosilicate glass bottles with ISO screw caps. Each glass beaker and scissors were rinsed twice with 15 mL of the extraction solvent mixture (dichloromethane-acetone-methanol (50:25:25)), and the two rinsates were pooled and reserved for use in the first extraction step.

Next, 150 mL of the extraction solvent mixture, together with the solvent rinsate cited above (approx. 30 mL), was added to each bottle holding the polymeric pieces. The caps were closed firmly, and the three ISO bottles with the corresponding pieces and solvents were placed simultaneously in an ultrasonic bath, Bransonic MH (Branson, Hospitalet de Llobregat, Spain), at 50 °C for 2 h. After cooling to room temperature, the mixtures of solvents were transferred to 250-mL volumetric flasks, while the pieces of the containers remained in the bottles. The pieces were then rinsed twice in the same bottle with 25 mL of fresh solvent mixture and placed in the corresponding volumetric flasks, which were brought to a volume of 250 mL, thus obtaining Extract 1 (E1).

The process was repeated twice with the same pieces using 180 mL of fresh solvent mixture, bringing them to final volumes of 250 mL to obtain Extracts 2 (E2) and 3 (E3), respectively (Figure 1).

After the three-step extraction of the three A halves per pesticide, the ISO bottles containing the pieces were left open horizontally in a fume hood at room temperature until complete evaporation of the solvents. Once the pieces were dry, three sets of pieces of approximately 4 g each were randomly selected from each ISO bottle. Each set was milled to powder separately in an Ultra Centrifugal Mill Retsch ZM 200 (Retsch, Düsseldorf, Germany) with a 12-tooth rotor measuring 99 mm in diameter and with a 0.5-mm mesh sieve. The first 2 g was discarded, and approximately 1 g from each set was weighed in 12-mL glass vials fitted with poly(tetrafluoroethylene) (PTFE)-lined caps; 10 mL of solvent mixture was added. The closed vials, located in a rack, were placed in an ultrasonic bath, and the same extraction process used for the 1 x 1 cm pieces was followed twice. Hence, two new extracts for each set of pulverized pieces were obtained, PWE1 and PWE2. In summary, for each half A of a single polymeric bottle, 3 consecutive extracts of the 1x1 pieces and 6 extracts corresponding to the two extractions from three sets of pulverized pieces were obtained. Overall, as there were 3 A halves per pesticide, a total of 27 extracts per pesticide were analysed.

The same procedure was followed for the analysis of glyphosate and imazamox, but in these cases the solvent mixture was methanol-water (50:50). Moreover, for glyphosate, all of the glass material was substituted by PTFE, polyethylene (PE) and polypropylene (PP) material.

2.3. Analysis of pesticides by UPLC-MS/MS

Each extract was analysed by evaporating 2 mL of the corresponding solution to dryness under nitrogen. The dry residue was dissolved with 0.5-5 mL of mobile phase to a convenient dilution depending on its concentration. The standards and samples were analysed separately by Ultra Performance Liquid Chromatography (UPLC), Acquity, from Waters Chromatography (Cerdanyola del Vallès, Spain), coupled to a photodiode array (PDA) 2996 detector (Waters) in conjunction with a mass spectrometer with a triple quadrupole analyser XEVO-TQ-S (Waters). The optimized chromatographic and mass spectrometer parameters for each pesticide are detailed in the Electronic Supplementary Information section.

Instrument control and data acquisition and processing were performed using MassLynx™ software version 4.1 (Waters, Milford, MA, USA).

3. Results and discussion

3.1. Designing the extraction procedure

In preliminary assays performed in triplicate, several containers from the collecting points of the Spanish national waste management scheme were sampled. The side walls of each container were selected, while the top and bottom parts were discarded. The selected portions were milled to powder, extracted and the pesticides (cypermethrin, dimethoate, glyphosate, imazamox, nicosulfuron and pendimethalin) analysed. However, the results (not shown) were inconsistent due to high differences among the repetitions. These differences were possibly due to the heterogeneous distribution of the pesticide remaining on/in the inner surface of the containers. Such a distribution occurs because, after the triple rinse, the containers were stored together in “big bags”, where they were positioned randomly. If a container is not drained completely before being placed in the large bag, the remaining water may end up anywhere in the bottle, or it may drip over the external surface of other bottles previously containing the same or a different pesticide. As a result of these dynamics, when the water evaporates, the pesticide residues may remain anywhere in the bottles.

Given the preliminary results obtained, we considered it necessary to analyse the whole container to test the persistence of the pesticide. This approach implies that all pesticide remaining in a container is removed irrespective of the inner or precise external area of the bottle surface to which it is adhered.

To design an extraction procedure under controlled conditions, three containers belonging to the same batch of the six pesticides, corresponding to commercially available formulations of cypermethrin, dimethoate, glyphosate, imazamox, nicosulfuron and pendimethalin, were acquired and processed in the laboratory. These pesticides were present in different commercial formulations and packaged in bottles made with different polymers (Table 1).

The pesticides remaining in the containers after the triple rinse and the air-drying under controlled conditions are to be likely distributed in the following way. One fraction remains attached to the surface while another is adsorbed to the inner wall of the containers or also absorbed into the polymeric wall. With the help of an appropriate solvent mixture, it is possible to remove the pesticide remaining on the surface of the inner wall. However, if a fraction of the pesticide has been adsorbed or absorbed within the polymer, a single cleaning with water will not be effective in removing it. The strength of the interaction between the pesticide and the polymeric wall is determined by the structure and properties of the pesticide, the nature of the polymer, the structure of the coatings, the composition of the commercial formulation, the external factors (e.g., temperature), the time between packaging and consumption, or the care in container manipulation (Delhom et al., 1996 and Fries and Zarfl, 2012).

The cypermethrin and pendimethalin formulations contained, among others, petroleum naphtha, and the dimethoate formulation contained cyclohexanone. The interaction between the pesticide and polymeric wall, the external factors contributing to it, and the time between packaging and consumption are difficult to measure; thus, the preparation of fortified samples to determine the percentage of recovery was not considered. These circumstances prompted us to design a method to achieve the maximum removal of the pesticide from the polymeric matrix.

In this regard, we considered an alternative extraction to release the total pesticide. This procedure involved the complete dissolution of the polymeric container (British Standard 2782, 2015 and Cheruthazhekatt et al., 2013). The operation was attempted with the A' strips. After three successive dissolution cycles of the A' strips, reduced to small pieces, in refluxing with xylene followed by precipitation by cooling, and the addition of methanol to the mixture, the amount of pesticide recovered was very low in

235 comparison with the proposed extraction procedure (results not shown). These results
236 may be attributable to the following: 1) complete sample dissolution requires higher
237 temperatures, which may lead to the decomposition of many pesticides; 2) when
238 containers are composed by distinct polymers, complete dissolution requires extreme
239 conditions, which increase the decomposition rate of the pesticide; and 3) the solution
240 is difficult to handle, requiring high volumes of solvent to dissolve a representative
241 amount of sample, and the persistence of a very low amount of the dissolved polymer
242 may interfere with the analysis. Therefore, on these premises, this option was
243 discarded.
244

245 **3.2. Selecting the extraction solvents**

246 The first step was to select the solvents to be used to remove the pesticides from the
247 containers. The solvents had to be suitable for a wide range of pesticides, which are
248 mainly neutral organic compounds that differ greatly in polarity. However, some
249 pesticides are inorganic compounds or organic compounds salts, with low solubility in
250 organic solvents and high solubility in water (Eldridge, 2015). Pesticides that are difficult
251 to solve, such as sulphur, were not considered. For the first group, because the main
252 polymeric compound in the containers was HDPE, the Hildebrand solubility parameter
253 (δ)—despite its limitations—was considered for solvent selection.
254 A compound or material will be soluble in a solvent when both the compound and the
255 solvent have a similar δ; this is the basis of the principle “like dissolves like”. For HDPE
256 containers, the δ value for HDPE (16.0 $MPa^{1/2}$) and the corresponding δ of the solvents
257 were considered (Brandrup et al., 2003).
258 Acetone has a δ value of 19.9 $MPa^{1/2}$, close to that of HDPE. Other solvents, such as n-
259 butyl acetate, cyclohexane, hexane, 1,1,1-trichloroethane and o-xylene have δ values of
260 17.3, 16.7, 14.8, 17.5 and 17.9 $MPa^{1/2}$, respectively, closer to that of HDPE than to
261 acetone. However, the objective was not to dissolve the polymer matrix but to expand
262 the polymeric chains, thus favouring the release and solving of the pesticides absorbed.
263 Moreover, acetone is a moderately polar solvent with high capacity to solve a wide
264 range of pesticides (EC. Pesticides, 2015, PPDB, 2015 and USDA, 2015).
265 To cover the entire range of pesticide polarities, in addition to acetone, the solvent
266 mixture comprised dichloromethane (δ= 20.3 $MPa^{1/2}$) and methanol (δ=29.1 $MPa^{1/2}$)
267 (Table 2), which are suitable solvents for non-polar and polar pesticides, respectively. In
268 addition, dichloromethane, like all halogenated solvents, is considered a good solvent

for HDPE. It is effective over 80 °C (Eldridge, 2015), and it also favours the removal of pesticides from the matrix. Moreover, dichloromethane, acetone, and methanol have boiling points below 65 °C, they are adequate to be removed prior to injection into UHPLC systems, their toxicity is known, and they are affordable common solvents in laboratories. All of these reasons prompted us to use them as extracting solvents in a (50:25:25) dichloromethane-acetone-methanol mixture. For the group of pesticides that included the salts of organic pesticides, the pesticides tested were imazamox ammonium salt (ammonium salt of 2-[(RS)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-5-methoxymethylnicotinic acid) and the glyphosate salt of isopropylamine (N-(phosphonomethyl)-glycinate of isopropylammonium); the extraction solvent in this case was a mixture of methanol-water (50:50).

Once the two solvent mixtures were selected, the extraction procedures were designed considering the characteristics of the respective samples.

3.3. Modelling the extraction procedure

As cited in the Material and Methods section, each half A of the containers was completely cut into 1 x 1 cm pieces, which were pooled and extracted three consecutive times with the aforementioned extraction mixtures at 50ºC for 2 h in an ultrasonic bath. This temperature increases the inner pressure in the ISO extraction bottle, thus accelerating the process. Moreover, for thermoplastic materials, a high temperature increases the solubility, diffusion rate, desorption, solubilisation kinetics, and mass transfer of the compounds (Barth and Majors, 2013).

An extraction time of 2 h may initially seem excessive for most pesticides, in which the recovery percentage of the second and third extractions falls under levels of units of percentage or less (Table 3) (considering that 100 % is the total amount of pesticide per gram of sample recovered in the successive extractions E1, E2, E3, PWE1 and PWE2). However, for cypermethrin, the second and third extraction reached recoveries of almost 10%.

Ultrasonication is a classical method for extracting analytes from samples (Chen et al., 2012 and Vandenburg et al., 1997). Three ISO extraction bottles can be processed simultaneously in an ultrasonically heated bath. Ultrasonic treatments have been reported of being potentially able to degrade some substances (Matouq et al., 2008). Consequently, two concentrations (high and low) of the standards for each pesticide (1.5 mL each) were exposed to the ultrasonication process under the same bath

conditions as the samples. No significant deviations of the standard concentrations were observed between the ultrasonicated and the calibration standards (results not shown). Other extraction methods such as Soxhlet, accelerated fluid extraction, microwaving or supercritical fluid extraction were discarded because they do not permit extraction of the whole container or because they could heat the sample excessively (Barth and Majors, 2013, Nerín et al., 1997 and Nerín et al., 2000).

While the percentage of pesticide recovered after each extraction of the pieces did not vary among the three A halves of the same pesticide, the amount of pesticide recovered varied widely. Especially for imazamox and glyphosate salts, the amounts extracted in the three repetitions differed by more than 3-fold, as evidenced by the standard deviation (Table 3). This observation was especially relevant among the three repetitions of E1.

These results reveal that the manual rinsing of bottles, even under controlled laboratory conditions, does not provide repeatability in the amount of pesticides remaining in the bottles because, in fact, each bottle is a different sample. Despite this, the amount of pesticide recovered was very low and far from the maximum legal threshold level established by the EU for a substance to be considered highly hazardous (0.1 g pesticide/100 g container) (Regulation EC 1272/2008, 2008). However, the extraction results for the three A halves, expressed as the percentage of the total amount of pesticide extracted, were similar in all cases, showing minor standard deviations. Hereafter, the percentage of pesticide recovered in a particular step will be indicated as that referring to the sum of the percentages of the five extractions.

To remove the pesticide absorbed on the polymeric walls of the containers, we considered pulverization. The milling of all pieces of each bottle into powder was discarded because it was too time-consuming and tedious and required a high amount of solvent. Instead, we performed random selection and pulverizing of a given weight of pieces from each half after E3. An important drawback of milling is the requirement to continuously decontaminate the milling unit. The previous extraction process to produce E1, E2 and E3, was useful to overcome this situation. By removing most of the pesticides in the extraction process, in combination with standard cleaning of the inside of the mill with solvents and discarding the first 2 g of the powder obtained, we did not detect contamination in the samples. The variation previously observed in the amount of pesticide in E1 was not perceived in the powder extraction.

Once most of the pesticides on the pieces were removed, mainly those adhering to the outer side of these pieces, we achieved high repeatability among the three repetitions

of the powder of half A for each container. Similarly, high repeatability was observed among the three containers for each pesticide (see Supplementary Material). The repeatability of these results allowed us to consider the selection of only a portion of the pieces to be pulverized maintaining enough ruggedness for this analysis. The percentage of pesticide extracted in the first powder extraction (PWE1) exceeded 10% of the total for cypermethrin, glyphosate and pendimethalin (Table 3). Except for glyphosate, the percentage in the second powder extraction (PWE2) diminished to unit percentage levels or lower in all cases.

High prevalence of the pesticide in the polymeric matrix during the extraction steps was observed for cypermethrin and glyphosate, while the prevalence of pendimethalin was lower. Otherwise, more than 90% of dimethoate, imazamox and nicosulfuron were removed in E1, while the recovery of these pesticides from powder was very low or even undetected. The different behaviour of these pesticides prompted us to consider the entire commercial product. Thus, for extraction efficiency, in addition to the pesticide, we considered the influence of the pesticide formulation and the composition of the inner wall of the polymeric container.

First, to assist in the interpretation of results the δ value of the pesticides was estimated using the method of the chemical group contribution through the following expression:

$$\delta = 2.0455 \frac{D \sum G}{M}$$

where “D” is the density, “G” is summation of Small’s molar attraction constants for each of the chemical groups present in the chemical structure of the pesticide, and “M" is the molar mass of the pesticide (Barton, 1991, Burke, 2015 and Hoy, 1970).

This may not be a fully rigorous method, but it is easy to apply in complex chemical structures and the obtained values when applying this equation provide a first approximation to the polarity of the compounds.

When a molar attraction constant for a chemical group was not previously described, the δ value was deduced from that of a solvent with an equal or very similar chemical group. Moreover, δ was estimated for the polymers comprising the containers and for the auxiliary components of the pesticide formulation when known.

The dimethoate bottled in HDPE internally coated with ethylene vinyl alcohol (HDPE-EVOH), the imazamox bottled in blended HDPE/PE-PA, and the nicosulfuron bottled in

HDPE exhibited good behaviour to the extraction process. The three pesticides were effectively removed from the polymeric material, mostly during E1 (Table 3).

Dimethoate is moderately soluble in water (25 g/L) and was prepared as an emulsion (400 g/L) containing cyclohexanone. Dimethoate exhibited an estimated δ of 22.0 $MPa^{1/2}$, and for cyclohexanone it was 19.8 $MPa^{1/2}$; both values were far from the 26 $MPa^{1/2}$ of the EVOH layer and the 16 $MPa^{1/2}$ of PE. Consequently, the interaction of this pesticide with the polymeric wall was low, as demonstrated by the experimental extraction.

Nicosulfuron showed the best recovery in E1, with almost irrelevant recoveries in successive extractions. This experimental result was fully consistent with the wide difference between the δ values of 28.8 and 16 $MPa^{1/2}$ for nicosulfuron and HDPE, respectively.

Cypermethrin was bottled in a COEX container. The manufacturer specified that the raw material was HDPE with a layer of PA polycaprolactame (AKULON XP36-C1®) with an adhesive resin (ADMER-NF408E®). Surprisingly, significant amounts of cypermethrin remained in the polymer during the extraction. This pesticide was formulated as an "emulsifiable concentrate containing petroleum naphtha". Petroleum naphtha is a mixture of various hydrocarbons and has a δ value between 15.2-18.7 $MPa^{1/2}$, a range very close to that shown by HDPE. The calculated δ for cypermethrin, 20.6 $MPa^{1/2}$, was far from that of HDPE but not sufficiently far from that of PA polycaprolactame (22.5 $MPa^{1/2}$) and naphtha. Despite the different layers in the container, the presence of naphtha in the formulation may favour diffusion of the pesticides into the polymeric wall.

Pendimethalin was in a PET container, and it was extracted in a similar way to cypermethrin although with somewhat greater efficiency, 81.4 % and 61.5 % in E1, respectively. The difference in δ values between the pesticide and PET (13.8 and 20.5 $MPa^{1/2}$, respectively) cannot explain the prevalence of the pesticide in the extractions. As observed for cypermethrin, the commercial formulation contained naphtha, which could favour the solubilisation of the pesticide into the polymeric matrix. As the difference in δ between the pesticide and PET was higher than for cypermethrin and PA in the COEX container, the diffusion effect of the pesticide was lower.

Imazamox and glyphosate were special cases; these pesticides are water-soluble salts, and their δ values cannot be considered for ionic compounds. Consequently, their behaviour must be interpreted in other terms. Imazamox is an emulsifiable concentrate with water, without further information provided by the supplier. As expected for ionic

405 compounds, the interaction of this pesticide with the HDPE/PE-PA container was low,
406 and thus E1 was almost complete (Table 3). It is well known that glyphosate adsorbs
407 strongly in soils, clays, and glass (Barton et al., 2011 and Druat et al., 1998) on the other
408 hand, there is a general consensus that HDPE, as a non-polar polymer, is a suitable
409 container material for a product comprising aqueous solutions of salts. However, our
410 experimental results question this understanding. Moreover, glyphosate has been
411 reported to interact with some polymers, as polyacrylamide (Ver Vers, 1999).
412

413 **3.4. Analysis of samples from farmers**

414 Once the extraction procedure had been established in controlled conditions and the
415 ruggedness in the percentage of recovery for each extraction was assessed, we tested
416 the method in the containers after their contents were used.
417 Samples were obtained from a residue collection point used by farmers in the municipal
418 area of Visaltia (Greece). The samples comprised individual bottles of crop pesticides
419 which had been triple rinsed by the farmers once emptied. Twenty bottles of 17
420 different pesticides, covering a wide range of polarities from ionic to semi-polar and
421 non-polar pesticides, were collected randomly from among the products most
422 frequently used in Mediterranean agriculture. For propargite and terbuthylazine, two
423 distinct formulations from different suppliers were analysed. The extraction procedures
424 explained above were applied to all samples, namely three consecutive extractions of
425 an entire bottle previously cut into 1x1 pieces (E1, E2, E3), without the cap, followed by
426 two extractions of 1 g each of the powder from randomly selected pieces (PWE1,
427 PWE2). As expected, the extraction efficiency and recovery percentages differed
428 between the products (pesticides within their corresponding containers) (Table 4).
429

A group of samples showed a predominant behaviour in 90 % of the cases (Figure 2), which could be considered regular. For this group, E1 allowed the recovery of most of the pesticide. Of these regular cases, dimethoate, lufenuron, propargite 1 and pyraflufen-ethyl were almost completely (95%) removed in E1, which constitutes an ideal behaviour (Figure 2).

For nicosulfuron, propargite 2 and sulcotrione, E2 and E3 allowed the recovery of a significant percentage, while the recovery of PWE1 and PWE2 was very low or the pesticide was not detected. In the remaining regular cases, the most frequent scenario was that the pesticides were extracted mainly by E1, but PWE1 allowed greater recoveries or recoveries similar to those achieved by E2 and E3. This was the case for carfentrazone-ethyl, cypermethrin, desmedipham, ethofumesate, fluometuron, glyphosate, phenmedipham, quizalofop-P-ethyl, quizalofop-P-tefuryl, and terbuthylazin 1 and 2.

All of these last cases demonstrate that the E extractions were insufficient to remove the pesticides, and a significant amount of these substances remained on the surface of the container or, more probably, in the polymeric matrix. In general, the amount of pesticide recovered in PWE2 was very low or not detected.

A second group of pesticides, accounting for approximately 10% of the samples, showed a distinct behaviour. In this regard, the E extractions removed a small amount of pesticide, and the extraction of the powder was thus unavoidable. Acetochlor and pendimethalin illustrate this scenario, and reveal that some conditions (e.g. solvents, auxiliary components) may allow high interaction between the polymeric matrix and certain pesticides.

Acetochlor and pendimethalin (Figure 2) had estimated δ values of 18.8 and 15.4 $MPa^{1/2}$, respectively, close to the 16 $MPa^{1/2}$ of HDPE; for acetochlor, the presence of petroleum naphtha (15.2-18.7 $MPa^{1/2}$) in the formulation also contributed to enhancing the interaction with the container material. The recovery of pendimethalin in the experimental extraction procedures (Table 3) was compared with that obtained from the farmers' samples (Table 4). Recovery was highly dependent on the container material. The δ value for pendimethalin was very similar to that of HDPE but not to that of PET (δ = 20.5 $MPa^{1/2}$); consequently, PET containers are more appropriate than HDPE for this pesticide (Figure 3).

463 The estimated value of δ (20.8 $MPa^{1/2}$) for nicosulfuron was closer to that of EVOH than
464 to HDPE. Consequently, HDPE would be more suitable for packaging this pesticide; this
465 conclusion is fully supported by the experimental data (Tables 3 and 4).
466 The cypermethrin used for the **modelling extraction procedure** and in the real sample
467 analysis was commercialized under two different formulations but in the same
468 packaging material. The recoveries found could be attributed to the differences in
469 solvents and auxiliary components (Table 3 and 4). The same can be assumed for the
470 two different formulations of propargite and terbuthylazine in the analysis of the real
471 samples from farmers (Table 4). In general, as expected, the presence of a PA or EVOH
472 coating on the inner surface of the bottle provided higher protection against the
473 diffusion of the pesticide into the polymeric matrix.
474

475 **3.5 Simplified extraction**

476 Given the general trend both in modelling and in the real sample extractions, we
477 considered shortening and simplifying the extraction procedure (Figure 1). As E1
478 removed over 80% of the pesticide in most pesticide/polymer combinations and the
479 extraction from the powder was required for some combinations, the extractions were
480 limited to E1 and PWE1. We compared the percentage of pesticide removed by
481 applying E1 followed by PWE1 versus the entire procedure described previously. For
482 this purpose, we applied the simplified extraction to half B of each bottle and the
483 amount of pesticide removed was compared with that corresponding to half A
484 subjected to full extraction (Table 5).
485 The Student t test showed no significant differences between the A and B halves in the
486 total amount of extracted pesticide. Although the simplified extraction procedure
487 cannot be extrapolated to any pesticide/package combination, it can be used as a
488 guideline when E2 has a very low recovery percentage. For routine analysis, the
489 adoption of the simplified extraction procedure, when this is well supported, is
490 recommended; it proves to be precise enough and it also allows considerable savings in
491 both time and solvent consumption.

492 **4. Conclusions**

493 Overall, and considering the present legal limits stablished for pesticides, the recycling
494 of the polymeric packages that have contained pesticides is feasible after the triple
495 rinsing. The triple rinsing of empty bottles removes most of the pesticides, achieving

levels below legal limit; this removal has been demonstrated for all cases with one exception. However, for some pesticide/polymer combinations, the significant amount of pesticide that persists within the polymer could be later released during recycling or reuse.

Depending on the future use of these polymers, besides being legally feasible, the product obtained after the recycling process has not to introduce risks. Given the need for methods to establish the hazard of containers that have held pesticides, we propose a reliable procedure to analyse these containers.

Solvents for neutral pesticides were selected considering the Hildebrand solubility (δ) of solvents and polymers together with those estimated for the pesticides. In some cases, the δ of the respective compounds explains the recovery of the pesticide during the extraction process.

Essentially, the proposed procedure is effective. The first extraction allowed the removal of most of the pesticides, and only in a few samples did a significant amount of pesticide remain within the polymer. In this latter situation, the pesticide was easily removed through one additional extraction of powder from the milled pieces. Based in this fact, the simplified procedure proved effective and no significant differences in the efficiency of pesticide removal were observed between applying the entire or the simplified procedure.

In summary, the present study evidences the prevalence of pesticides in the agronomic post-consumer polymeric packages and meets the demand of public institutions and private companies in having a procedure to control the suitability of the pesticide packages to be reused. The availability of checking procedures is a need for implementing an environmentally friendly circular economy and the method may also help in designing suitable packaging for specific formulations.

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Note

All procedures involving the handling or transference of pesticides or solvents must be conducted in a fume hood, and personal protection measures must be taken.

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Tables

Table 1

Characteristics of the tested pesticide containers[a]

Content (pesticide)	Polymeric composition[a]	Commercial formulation
Cypermethrin 100 g/L	Coextrusion multilayer (COEX): HDPE/PA (nylon 6)	Emulsifiable concentrate containing petroleum naphtha
Dimethoate 400 g/L	High density polyethylene-Ethylene vinyl alcohol (HDPE-EVOH)	Emulsifiable concentrate containing cyclohexanone
Glyphosate, isopropylamine salt 360 g/L	High density polyethylene (HDPE)	Water soluble
Imazamox, ammonium salt 400 g/L	(High density polythylene-Polyethylene/polyamide blended (HDPE/PE-PA)	Concentrate emulsifiable with water
Nicosulfuron 40 g/L	High density polyethylene (HDPE)	Soluble concentrate
Pendimethalin 330 g/L	Poly(ethylene terephthalate) (PET)	Emulsifiable concentrate containing petroleum naphtha

[a]: According the manufacturer's specifications

Table 2

Estimated Hildebrand solubility parameters (δ) for the tested pesticides and solubility in the selected solvents

	δ	Solubility (g/L, 20 ºC)			
Commercial name		**Water (pH 7)**	**Methanol**	**Acetone**	**Dichloromethane**
Cypermethrin	20.6	<0.001	> 450	> 450	> 450[a]
Dimethoate	22.0	25[b]	>300		>300
Glyphosate		11.6			
Imazamox		116[b,c]	67		
Nicosulfuron	28.8	0.120[c]	4.5[d]	18	160
Pendimethalin	15.4	<0.001		800	800

[a]: in chloroform, [b]: pH 5, [c]: 25 ºC, [d]: in ethanol.

Table 3

Relative percentage and amount of pesticide recovered from the containers with the two-step extraction: E1, E2 and E3 successive extracts from 1x1 cm container pieces; PWE1 and PWE2 successive extracts from container powder

	Relative percentage recovered ± standard deviation (n=3)					Total amount recovered (µg/g)[a]
Pesticide	E1	E2	E3	PWE1	PWE2	
Cypermethrin	61.5±3.10	7.7±1.19	7.1±1.15	19.9±1.30	3.8±0.44	4.185±0.6376
Dimethoate	91.4±3.00	4.9±1.45	2.4±1.14	1.3±0.42	0.0±0.01	0.006±0.0026
Glyphosate	68.0±9.99	3.6±0.15	2.1±0.01	14.7±2.95	11.6±3.05	26.52±11.881
Imazamox	98.4±0.79	0.6±0.13	0.4±0.22	0.4±0.02	0.1±0.00	8.935±5.3114
Nicosulfuron	99.0±1.00	0.9±0.20	0.1±0.02	0.0±0.03	0.0±0.00	4.637±0.6812
Pendimethalin	81.4±2.05	4.0±0.38	2.8±0.31	11.0±1.49	0.8±0.14	30.36±2.3884

[a]: max. level in EU: 0.1 g pesticide/100 g container, or 1000 µg/g.

Table 4

Pesticide concentration in containers obtained from farmers after consecutive extracts from container pieces (E1, E2 and E3), followed by consecutive extracts from the container powder (PWE1 and PWE2).

	Pesticide recovery (%)					PCC[a]	TR[b]	
Pesticide	**E1**	**E2**	**E3**	**PWE1**	**PWE2**		**µg/g**	**g/100 g**
Acetochlor	22.3	12.4	9.70	50.4	5.10	HDPE	455.1	0.045
Carfentrazone E	94.7	3.70	0.00	1.40	0.10	HDPE/ EVOH	239.2	0.024
Cypermethrin	86.3	8.70	1.50	3.20	0.20	PE/PA	10.00	0.001
Desmedipham	89.6	0.90	0.00	8.40	1.10	PE/PA	0.233	2.3E-5
Dimethoate	97.1	2.60	0.30	0.10	0.00	PE/PA	6.195	6.2E-4
Ethofumesate	93.7	1.90	0.60	3.60	0.20	HDPE	1181	0.118
Fluometuron	92.2	3.00	0.80	3.80	0.30	HDPE	46.48	0.005
Glyphosate T	75.6	13.2	2.50	5.10	3.60	PET	38.66	0.004
Lufenuron	95.6	3.50	0.80	0.10	0.00	HDPE/ EVOH	2.987	3E-4
Nicosulfuron	82.4	13.0	3.60	0.90	0.01	HDPE/ EVOH	3.792	4E-4
Pendimethalin	26.2	12.1	8.90	47.8	5.00	HDPE	662.5	0.066
Phenmedipham	87.2	3.20	0.50	7.90	1.20	PE/PA	0.248	2.5E-5
Propargite 1	95.6	3.10	1.10	0.10	0.00	PE/PA	48.05	0.005
Propargite 2	86.8	9.10	3.70	0.40	0.00	PE/PA	25.78	0.003
Pyraflufen-E	99.7	0.30	0.00	0.00	0.00	HDPE/ EVOH	125.9	0.013
Quizalofop-P-E	61.7	10.3	8.10	19.2	0.60	PE/PA	25.42	0.002
Quizalofop-P-T	80.3	8.90	3.60	6.70	0.40	PE/PA	1.780	1.8E-4
Sulcotrione	88.1	7.30	3.90	0.70	0.10	HDPE	7.757	7.7E-4
Terbuthylazine 1	77.3	5.90	2.30	14.2	0.30	HDPE	71.20	0.007
Terbuthylazine 2	86.9	5.40	2.30	4.90	0.40	HDPE	58.73	0.006

[a]: Polymeric composition of container. [b]: Total amount of pesticide recovered (µg/g and g pesticide/100 g of container.

Carfentrazone E: Carfentrazone ethyl. Glyphosate T: Glyphosate trimesium. Pyraflufen-E: Pyraflufen-ethyl. Quizalofop-P-E: Quizalofop-P-ethyl. Quizalofop-P-T: Quizalofop-P- tefuryl

Table 5

Pesticide extracted following the full procedure (three consecutive extractions from the container pieces followed by two consecutive extractions of powdered pieces) versus the pesticide extraction with the simplified procedure (one extraction from the container pieces followed by one extraction from powdered pieces)

Pesticide	**Half**	**Extraction Average (µg/g) (n=3)**	**sd**	**t (α=0.05)**
Cypermethrin	A	4.185	0.6386	-0.83 (2.78)
	B	3.726	0.7126	
Dimethoate	A	0.006	0.0026	0.46 (2.78)
	B	0.007	0.0023	
Glyphosate	A	26.52	11.881	0.10 (2.78)
	B	25.29	16.497	
Imazamox	A	8.936	5.3114	0.38 (2.78)
	B	7.516	3.5856	
Nicosulfuron	A	4.637	0.6812	0.70 (4.30)
	B	3.680	2.2503	
Pendimethalin	A	30.36	2.3883	0.06 (4.30)
	B	30.07	7.4011	

Figure 1
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Figure 1

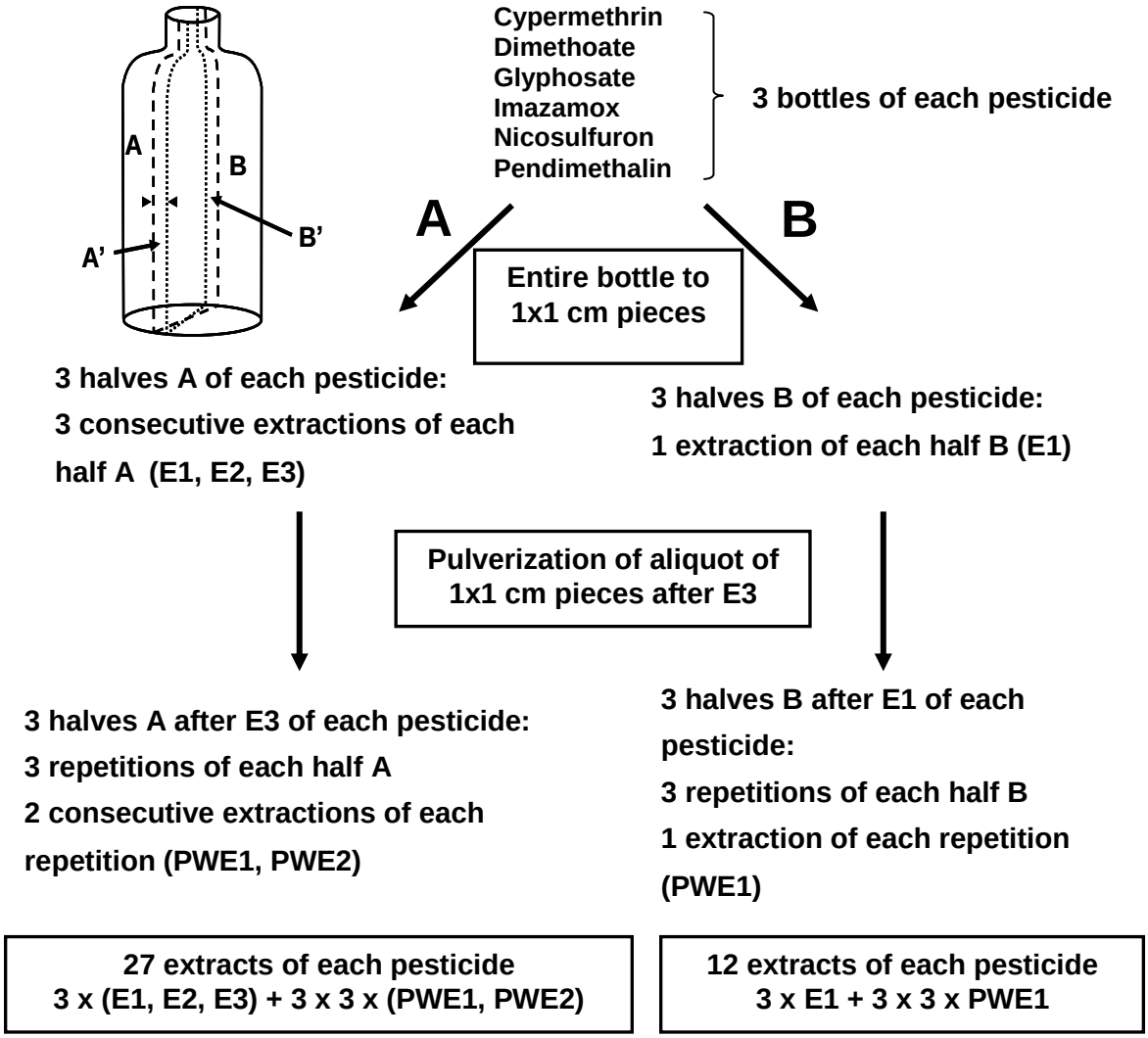

Fig. 1 Extraction procedure of pesticides remaining in the triple-rinsed containers. A: entire extraction procedure; B: simplified extraction procedure; A': extraction by bottle strip solubilisation; B': bottle strip for counter analysis. E1, E2, E3: successive extractions of 1x1 cm pieces of every half bottle sample. PWE1, PWE2: successive extractions of a pulverized aliquot of the 1x1 cm pieces after E3.

Figure 2
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Figure 2

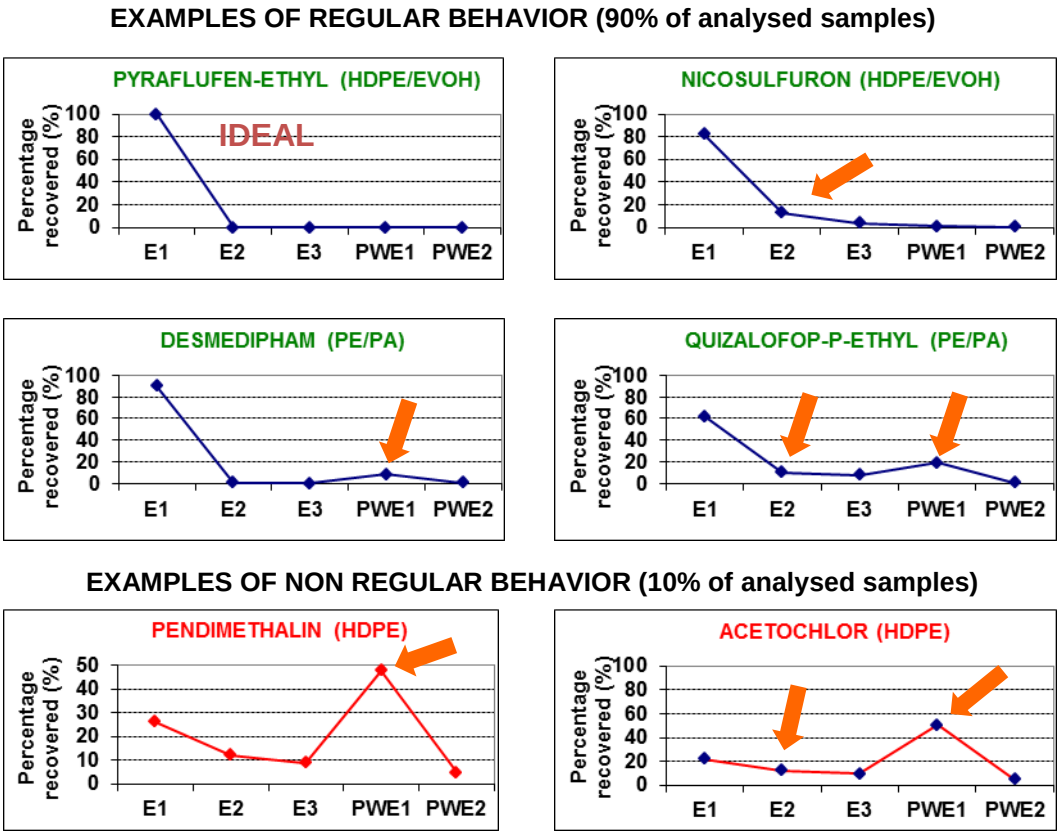

Fig. 2 Extraction behaviour of the pesticide residues from containers obtained from farmers. The arrow indicates deviation versus ideal extraction behaviour.

Figure 3
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Figure 3

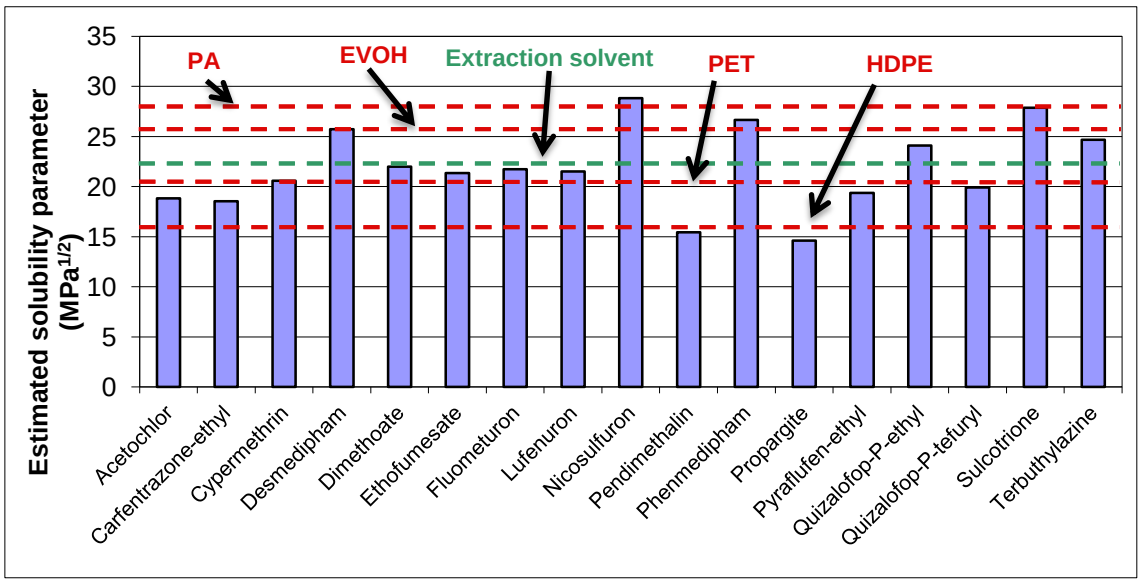

Fig. 3 Estimated solubility parameters (δ)of the pesticides and the solubility parameters of the solvent mixture and the container materials.

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